NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Report 32-1211

The Structure of the Grain Boundary in Ceramics

E.C. de Wys
M.H. Leipold

GPO PRICE $ _____

CFSTI PRICE(S) $ _____

Hard copy (HC) _____

Microfiche (MF) _____

ff 653 July 65

N 68-18019
(ACCESSION NUMBER) (THRU)
16 1
(PAGES) (CODE)
CR-93366 18
(NASA CR OR TMX OR AD NUMBER) (CATEGORY)
FACILITY FORM 602

MAR 1968
RECEIVED
NASA STI FACILITY
INPUT BRANCH

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

February 15, 1968

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Report 32-1211

The Structure of the Grain Boundary in Ceramics

E.C. de Wys
M.H. Leipold

Approved by:

Howard E. Martens

Howard E. Martens, *Manager*
Materials Section

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

February 15, 1968

TECHNICAL REPORT 32-1211

Copyright © 1968
Jet Propulsion Laboratory
California Institute of Technology

Prepared Under Contract No. NAS 7-100
National Aeronautics & Space Administration

Contents

I. Introduction 1

II. General Discussions 2

A. Theoretical Expectations 2

B. Experimental Approaches 3

1. Hardness testing 3

2. X-ray diffraction 4

3. Optical microscopy 4

4. Electron microscopy 6

5. Other techniques 6

III. Experimental Results 6

A. Micrography 6

B. Preferred Orientation 9

C. Von Laue Pattern 9

D. Light Microscopy 9

IV. Conclusions 9

A. General Conclusion 9

B. Possible Future Work 11

References 11

Figures

1. The outline of the total grain is revealed but only the top substructural region is approximately fulfilling the Bragg diffraction requirements . . 6

2. X-ray micrography showing diagonal extended edge dislocations, one of which shows a curved kink 7

3. X-ray micrograph showing a diagonal edge extended dislocation with composite jog 7

4. X-ray micrograph showing a diagonal edge dislocation that reflects away from grain boundary region 8

5. Enlarged image of the region of Fig. 4 showing bent edge dislocation 8

6. Bright field image of MgO grain boundary 9

7. Phase contrast image of MgO grain boundary 9

8. Bright field image of MgO grain boundary 10

9. Phase contrast image of MgO grain boundary 10

PRECEDING PAGE BLANK NOT FILMED.

Abstract

As part of a program to determine the role of the grain boundary in the behavior of polycrystalline ceramics, research has been conducted to directly observe the atomic structure and microstructure of the grain boundary in a typical polycrystalline ceramic (MgO). Various experimental techniques were considered and discussed, and preliminary results, using several techniques, were obtained. Termination of the entire effort prevented more complete findings and development of a useable model of grain boundary structure. However, the preliminary results did indicate extreme complexity in the grain boundary structure of the high-purity magnesium oxide samples. Advanced X-ray techniques and quantitative optical microscopy also appeared to be quite useful.

NASA
FORMAL
REPORT

FF No. 665 Aug 65

The Structure of the Grain Boundary in Ceramics

I. Introduction

Much of the behavior of polycrystalline ceramics is controlled by the presence of grain boundaries. Diffusion at low and moderate temperatures is a grain-boundary-controlled process. Mechanical deformation at high temperatures in ceramics is largely by grain boundary sliding. Mechanical behavior at lower temperatures is well understood, but certainly grain boundaries are involved. An extensive program directed toward the understanding of the nature and influence of grain boundaries on ceramic behavior had been under way at the Jet Propulsion Laboratory (JPL). (See Ref. 1.) This report describes the results of that phase of the program directed toward determination of grain boundary structure. Unfortunately, conditions did not permit the completion of this activity, and consequently, these results are incomplete. They represent the initial evaluation of the problem of the structure of grain boundaries in ceramics, the selection of applicable scientific techniques, and the very preliminary results that were obtained from these techniques. Finally, conclusions that were evident are noted, and suggestions and directions for continuation of the program elsewhere are presented.

Detailed knowledge of the structure of real grain boundaries in ceramics is extremely meager. There are several models for the structure: (1) dislocation array, (2) viscous layer, (3) island of fit and misfit; but experimental verification of these models or development of a different, more suitable model appears to be lacking. Further, there is a wide disparity in thinking concerning the zone of influence of a grain boundary in a ceramic material, depending on the source of the information on which inferences of size are based. For example, diffusion studies and micro hardness studies suggest numbers of microns for grain boundary size, while application of basic Griffith–Orowan theory to intracrystalline fracture studies suggests tens of Ångstroms.

The complete lack of direct observations of the structure of grain boundary in the literature provides no real basis for designing an experimental program which in our

study was also limited by the equipment available. Consequently, the approach used and reported here was to apply the classic techniques for study of microstructure and atomic structure and to use as many of these techniques as could be obtained to permit cross-correlation of the results.

II. General Discussions

A. Theoretical Expectations

Uncontaminated grain boundaries may be regarded as less-ordered, narrow areas misoriented between more perfect crystalline regions. The misorientation may be accommodated by means of atomic misfit at the boundaries, or in addition by elastic deformation extending over areas several atomic spacings in extent. The latter cannot, alone, accommodate the total extent of the misfits, but, in addition, the grains must be interconnected by line and screw dislocation type of slip regions. For an ionic crystal with a face centered cubic structure (Fm3m) such as MgO, the persistent requirement to maintain electrical neutrality along any line dislocation imposes the stringent condition that the additional $(n+1)$ half plane shall not disturb this neutrality. In MgO the shortest lattice vector connecting ions of the same electrical sign is along the [110] direction. The length of such a vector is $a_\circ \sqrt{2}$ or 5.95 Å. Cubic strongly ionic crystals usually glide along [110] direction, parallel to rows of equally charged ion. The glide is therefore normally 110 although in some instances the 100 planes will act as glide planes. An edge dislocation having an 011 glide plane, lying along the [100] direction and with a Burgers vector along [011] direction will normally have a double 011 type of plane perpendicular to the 011 glide plane as the extra half plane above the glide plane. Such a vector is therefore the $(a/2)$ [110]. The dislocation axis will show, in general, a neutral jog in order to preserve neutrality near the glide plane. Charged jogs would tend to interact strongly with point defects. In addition to edge dislocations, it is suspected that screw dislocation in the 111 planes will occur in *Fm3m* crystals.

For a tilt boundary, which is built up out of parallel pure edge dislocation with a Burgers vector b perpendicular to the boundary, the orientation difference is a simple rotation over the angle θ where

$$2 \sin \frac{\theta}{2} = \frac{b}{L}$$

where L is the distance between dislocations or coherent regions. For a small angle twist boundary the value for θ is given by

$$\sin \theta = \frac{b}{L}$$

For either, the energy per dislocation per unit length would approximate

$$E_d = \left[\frac{3 E_y K b^2}{4\pi}(1-\delta)\right] \ln \frac{L}{b_\circ}$$

The energy of the wall per unit area would be

$$E_w = \left[\frac{3 E_y K b}{4\pi}(1-\delta)\right]\left(\ln \frac{b}{b_\circ} - \ln \theta\right)$$

For the above E_y = Young's modulus, K = bulk modulus, b = Burgers vector, δ = Poisson's ratio, and $b_\circ$ normally has a value between ½ to $2b$. These energies may be compared with experimentally determined data obtained by measuring the angle made by three boundaries meeting along a common line. In general, a dislocation moving towards a free surface will be attracted to it by an image force equal to

$$F = -\frac{3 E_y K b^2}{4\pi L}$$

The presence in the grain boundary region of a material with higher E_y and K values will cause the dislocation to be repelled when it has approached to within a distance that is smaller than the total thickness of the boundary region itself.

Since each dislocation is surrounded by an elastic stress field that will strongly interact with one related to another dislocation, the result may well become a metastable multidislocation configuration. Since any applied stress required to move a dislocation must therefore exceed that of the total system of interlocked stresses, a given boundary region possessing such features will appear to be hardened. In the case of locally occurring coincidence-type lattices separated by zones of misfit, the presence of interlocked dislocations would cause local hardening and prevent dislocations from gliding through the boundary interface.

In real polycrystalline materials, the existence of impurity concentrations creating potential diffusion mechanisms must be considered. In general diffusion along grain

boundaries may be expressed by the general Arrhenius form

$$D_b = D_\circ \exp \frac{-E_b}{Kt}$$

where $D_\circ$ is the self diffusion coefficient along the boundary, E_b = activation energy of self diffusion, which usually has a value of about one half that required for volume diffusion. In small angle boundaries in metals the diffusivity is proportional to the misorientation angles. Dispersed line dislocations act as passageways of easy diffusion, which might show up as narrow linear lamellae inside grain boundaries. The slipping of two closely adjacent dislocations of opposite Burgers vectors may form "dipoles." These dipoles will achieve minimum separation if their respective lengths are greater than the distances apart in the dipolar region. The resulting dipoles will cause the lamellae to break up into loops.

This mass transport of impurity atoms by diffusion may cause oversized atoms to concentrate in regions of tension around the dislocation, while the undersized substitutional atoms will be in compressional areas. The resulting release of distortions around the dislocations could result in local strain aging with associated low-stress activation energy of dislocation movement.

In discussing diffusion rates in crystalline regions of actual MgO, it must be remembered that the presence of various kinds of impurities found in real polycrystalline systems creates, at least temporarily, multicomponent systems. In such a system, at diffusion temperatures, liquid-like diffusion systems could be generated which will thoroughly mask any potential effect of misorientation angle. Aspects of electronic and chemical concentration gradient in local multicomponent system may become more significant, as may be, for that matter, the effect of intercrystalline pressure gradients. It would seem that the absence or presence of impurities within the grain boundary region itself should have an effect on any diffusion rate along these disordered regions. Any recrystallization brought about by mass transport of atoms could create, locally, a coincidence type of sublattice ordering. Such a sublattice, at the boundary, has the same symmetry but a somewhat extended unit cell.

The presence of numerous point defects related to a concentration of vacancies and foreign atoms may locally cause the formation of highly disordered regions, with vitreous characteristics, surrounding more coherent substructural areas located between linear dislocations.

It is clear from the above that both geometrical and chemical discontinuities may exist simultaneously at the grain boundaries. Any process related to the above which will lower the free energy of the system will tend to be locally dominant. Since it may be demonstrated that for a solid, the change in free energy (among other parameters) is proportional to any change in the surface tension; it follows that on prolonged recrystallization the 100 and 111 planes of a face-centered cube will tend to become the grain boundary interface. The above follows from the fact that these planes possess the highest reticular density of structural elements to which the surface tension is inversely proportional.

For such very low-energy coherent-type boundaries, the value of the surface tension will change rapidly with orientation. It must be assumed, from the above, that in terms of chemical discontinuity any solute ion that will lower the value of the surface tension will readily diffuse into the boundary region resulting in selective compound formation or, in the case of polar crystals, additional strain hardening. It would appear that a back-streaming of other foreign ions from the grain boundary should have a distinct possibility of existence. Such a process should create a region beyond the grain boundary for distinct reaction between these ionic species and various solute ions moving toward the grain boundaries.

B. Experimental Approaches

In reality, the problem of observing the structure of grain boundaries resolves itself into the application of conventional structure-sensitive techniques but on a microscale commensurate with the zone of influence of the boundary. Many such micro techniques exist and have been applied to some extent while others have not. In this report, the application of many such techniques will be discussed in turn.

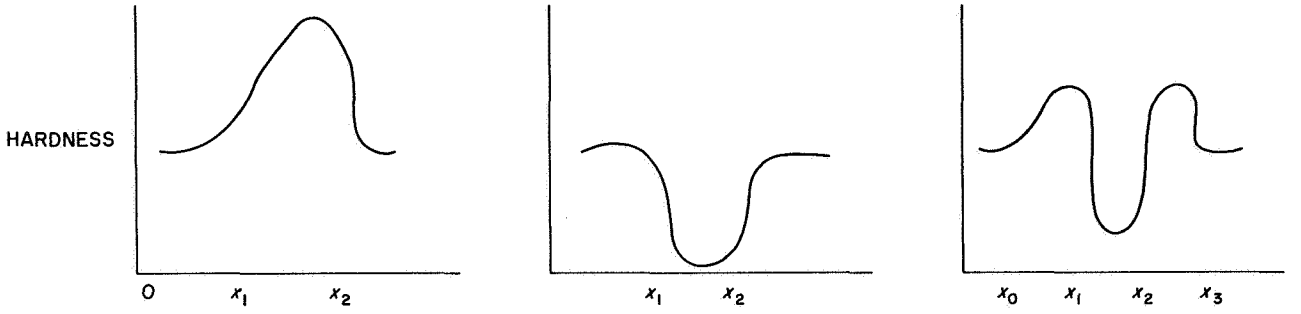
1. Hardness testing. The theories just discussed tend to indicate that numerous dislocated regions in the grain boundary would, due to strain hardening, exhibit a hardness value in excess of that of the less strained grain interior.

Other areas with disordered vitreous aspects and solute impurity ions may indeed be softer than the grain region.

The tendency of the grain boundary to reject impurity ions that tend to raise the surface tension could create a stressed barrier zone near the boundary consisting of a large number of these rejected ions. This barrier could

exhibit a hardness unlike that of the grain interior or the grain boundary.

It would appear therefore that hardness curves could show aspects of the three curves shown in sketch A.



GRAIN BOUNDARY BETWEEN x_1 AND x_2 SHOWING STRAIN HARDENING.

GRAIN BOUNDARY BETWEEN x_1 AND x_2 SHOWING DISORDERED VITREOUS STATE.

GRAIN BOUNDARY BETWEEN $x_1 - x_2$ AND SOLUTE ZONE BETWEEN $x_0 - x_1$ AND $x_2 - x_3$

Sketch A

Certainly this approach has provided and can continue to provide inferences on grain boundary structure.

2. X-ray diffraction

a. Micrography. One of the pertinent techniques to be used would be the X-ray diffraction micrography technique as discovered by W. Berg and later on refined by Barrett. This technique should clearly reveal subgrain structure as well as the defect structures within. The actual sites of the individual dislocation on the surface should be clearly revealed. The image contrasts observed on the X-ray film is related to the misorientation of subgrains, inhomogeneous lattice strain, orientation of the defect structures, orientation of the individual crystals in the polycrystalline aggregate, as well as excessive surface contours that cause partial absorption of the primary X-ray beam.

The orientation of grains on either side of a grain boundary is determined by a crystal rocking analysis somewhat similar to that used by Sigmund Weismann. A similar technique can be used on the grain boundaries themselves.

It is to be expected that with polycrystalline MgO, Berg–Barrett photographs should indicate the presence of substructures, linear dislocation and various angles between grains and any atomic planes within the grain boundaries.

The linear dislocation for MgO should show some jog patterns and in some instances penetrate the grain boundaries, while in some instances bend away from the boundaries.

Since the dislocation with the Burgers vector (greatest strain) normal to the planes, satisfying the Bragg's condition will have the greatest image contrast compared with those that have their Burgers vector lying in the diffracting planes; it is expected that a distinct intensity difference will be noted between sets of dislocations. The screw dislocation will probably show some cross slipped structures.

b. Preferred orientation analysis. On the basis of the theoretical discussion presented, it is to be expected that sintering a polycrystalline MgO, a preferred orientation pattern will tend to develop with low index *hkl* value, such as 100 planes. In order to detect an orientation effect, it would be necessary to use a high-resolution 2 deg rotation pole figure device.

c. Von Laue pattern. The grain boundary region has associated with it a field of dilatation, angular misorientation, and possible variable phase composition characteristics. Precision lattice parameter measurements (indicating crystal lattice dilatation) and detailed analysis of the Von Laue spot geometry should reveal details concerning the grain boundary.

3. Optical microscopy. For isotropic media such as MgO and highly disordered grain boundary regions, the index of refraction relationship may be described by the standard relationship:

$$\frac{(n^2-1)}{(n^2+2)} \cdot \frac{M}{\rho} = X_1 (\tfrac{4}{3}\pi N_\circ \alpha_1) + X_2 (\tfrac{4}{3}\pi N_\circ \alpha_2) + \cdots$$

From the above it should be clear that the index of refraction n of the grain boundary will vary as various impurities (X_i) with various polarizabilities (α_i) are added to the grain boundary region or the MgO crystal itself. It is therefore expected that the grain boundary region will have in general an increase or decrease in index of refractivity as the cation refractivity increases or decreases. The presence of calcium ions with an ion refractivity significantly higher than that of Mg would tend to raise the index of refraction. In contrast the presence of Si would tend to decrease the index of refraction. The effect of Al ions should not have a pronounced effect. The presence of K, Li, or Na should cause an increasing reduction of index of refraction. It would appear therefore that the presence of any compounds (whether as crystals or amorphous) such as $KAlSi_3O_8$, $NaAlSi_3O_8$, $CaAl_2Si_2O_8$, or SiO_2 at the grain boundary would cause an overall local index of refraction reduction at the grain boundary. Since the presence of a proton reduces the polarizability of an oxygen ion, the effect of any $Mg(OH)_2$ formation would tend to reduce the index of refraction significantly.

The effect of any stress at the grain boundary sufficient to decrease the looseness of the electron shell system will reduce the index of refraction. Since strain in a grain boundary tends to be directional, the index of refraction will be affected directionally, and a birefringence effect parallel to boundary is to be expected.

Since the atoms at a triple junction are at a higher free energy state than those along the grain boundaries or inside the grains, the triple junction will tend to be below the elevation levels of the two latter cases. The result will be a reduction in optical path length at the triple junction.

From the above, it is suspected that the grain boundary interior will tend to have linear regions with predominantly shorter optical paths than those within the MgO grain interiors. The presence of a high predominantly local concentration of Ca ions will tend to create a region with higher index of refraction however.

It is clear that any optical techniques allowing measurement of optical path differences at high resolving powers would be well suited for examination of grain boundary regions.

The effective lateral resolution of a microscope lies between λ/NA to $\lambda/2NA$, which with modern numerical apertures (NA) up to 1.44 is sufficient to resolve 3000 to 5000 Å details within the observed MgO grain boundary.

In bright field transmitted light illumination of a normal thin section an index of visibility of 3% corresponding approximately to a phase difference of 60 deg is sufficient for observational purposes of index of refraction differences of 0.03 within the grain boundary. This should be barely sufficient for the detection of any expected complex compounds but not ideal for expected changes due to impurity concentrations.

By means of phase contrast, a phase difference of 10 deg or an index of refraction difference of 0.005 is clearly visible, which in combination with a high numerical aperture lens would be a more realistic approach to obtaining details other than compounds within grain boundaries. The amount of contrast visible would be expressed by the relationship:

$$\gamma = \frac{1 - \cos \Delta p - D^{1/2} \cdot \sin \Delta p}{1 + D - \cos \Delta p - D^{1/2} \cdot \sin \Delta p}$$

where Δp is the phase difference and D is the absorption of the phase retardation rings in the objective.

For actual measurement of the total path difference a double or multiple beam interferometer would be used. This approach should quantitatively indicate the changes in index of refraction or depression of a region within the grain boundary. This method should be capable of resolving depressions of approximately 40 Å.

It is fully expected that these methods will clearly show numerous and various optical path difference in the MgO grain boundary regions.

In order to emphasize those areas that are not truly isotropic along the grain boundaries, crossed circular polarizers may be used. The optical path difference (Γ) for the anisotropic regions may be determined by the relationship:

$$I = \frac{I_0 \sin^2 \pi\Gamma}{\lambda_0}$$

For this work a precision photomultiplier readout system would be needed.

In addition to the above microscopic techniques it is felt that standard chemical microscopical techniques could be used to reveal a broad range of chemical inhomogeneities in the grain boundary region. Some prior work by means of electron beam microprobe studies as part of this program have indicated the existence of chemical

separation of some cations to the present limits of detection (Ref. 2). Other work remains in progress and is being reported elsewhere.

4. Electron microscopy. The use of a high-resolution electron microscope for the study of dislocations was of course considered since it is indeed a classical approach. In addition selected area diffraction of the grain boundary region would have supplied additional information concerning the progressive change in structure from an ordered lattice to a progressively distorted region. In addition the existence of any distinct phase changes would have been determined.

5. Other techniques. Consideration could be given to such approaches as resonance and Mössbauer techniques to provide information concerning the electronic and magnetic environment of atoms at grain boundaries.

III. Experimental Results

The selection of initial approaches to the problem of grain boundary structure was based on the use of existing equipment. This preliminary approach permitted selection of criteria for procurement of more applicable facilities. The available items included a double-crystal diffractometer built by the New Brunswick Scientific Co. and a microfocus X-ray generator. Some initial pole figure work was done by means of manual operation of a single-crystal goniometer head-mounted on an XRD5 model spectrogoniometer. Additional relevant equipment such as an X-ray micrographic camera and a micro Laue unit were ordered. The use of these was prevented by termination of this activity. Hardness testing was not attempted since some available work (Ref. 3)[1] indicated that although effects were observed, interpretation was not obvious. Some phase contrast and optical interferometry was done during preliminary tests at the showroom of Max Erb Co. This type of equipment was ordered but cancelled due to project termination.

A. Micrography

The previously discussed X-ray micrography was done with the Berg–Barrett attachments to the double-crystal goniometer. A high-power microfocus generator with a line and spot type of filament and copper target and nickel filter was employed as a source of X rays. Type M film and high-resolution plates were employed. The 200 reflection was used to obtain X-ray micrographic images from a polycrystalline MgO sample. The sample was stepped through various minutes of arc through the Bragg angle for the 200 reflection.

[1]Also private communication from P. F. Becher, State University of North Carolina, Raleigh, N.C.

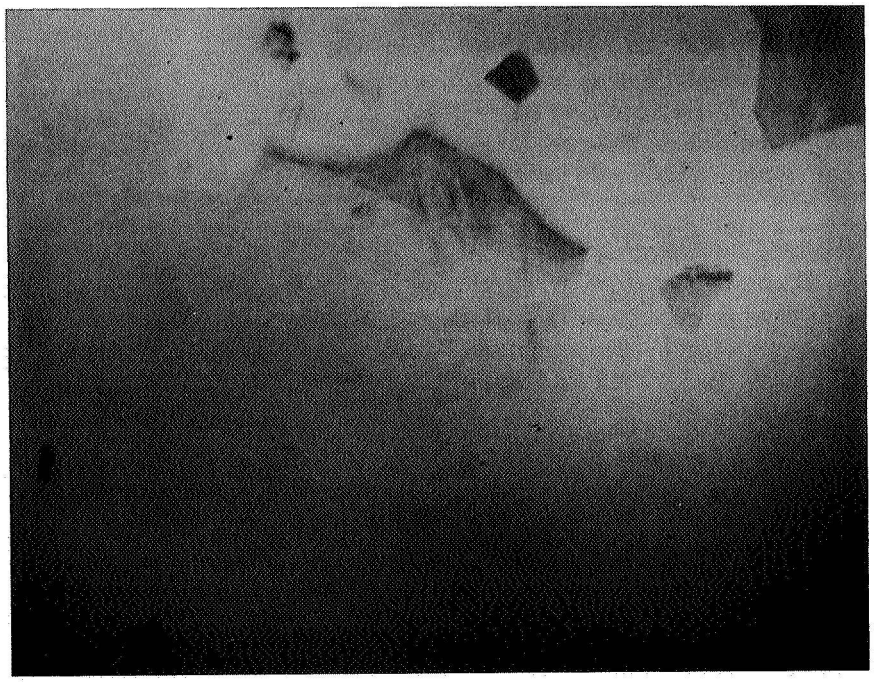


Fig. 1. The outline of the total grain is revealed but only the top substructural region is approximately fulfilling the Bragg diffraction requirements

The X-ray micrographs clearly reveal the presence of substructural regions within the grains. These substructural regions appear to be bounded by edge dislocations (Fig. 1). Some of the edge dislocations with a $a/2$ [110] Burgers vectors are of the extended type (Fig. 2). In one instance the dislocation has a curved kink indicating the effect of the densely packed minimum energy directions in the lattice. In Fig. 3 one of the dislocations shows

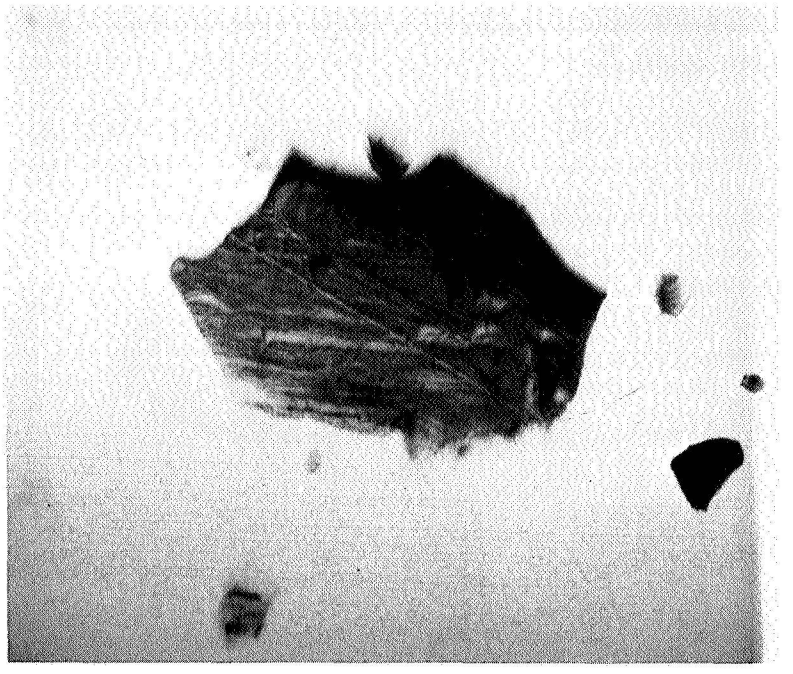


Fig. 2. X-ray micrography showing diagonal extended edge dislocations, one of which shows a curved kink. The broad white bands are regarded as slip planes

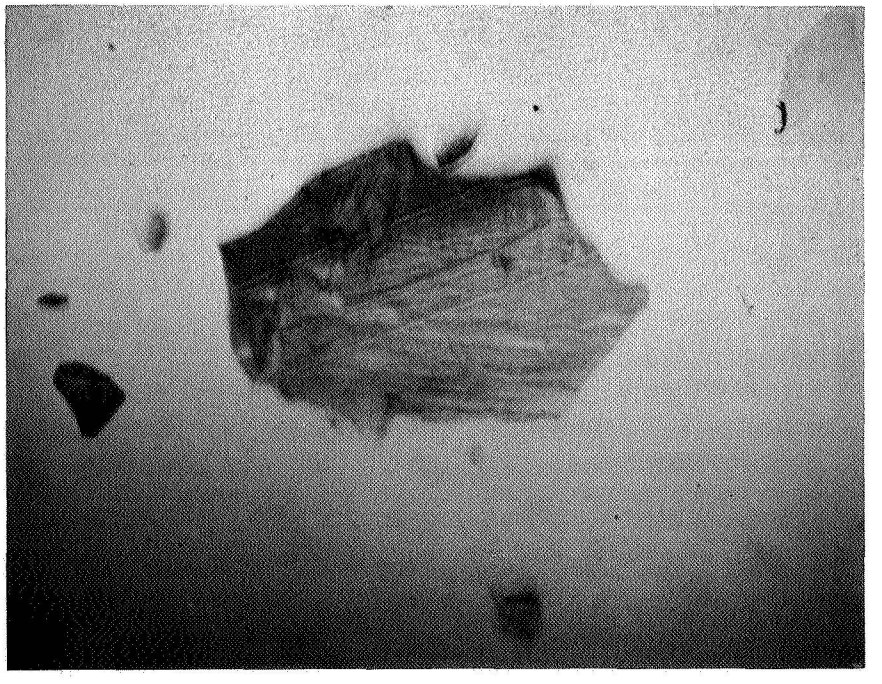


Fig. 3. X-ray micrograph showing (at the top) a diagonal edge extended dislocation with composite jog

the predicted composite jogs. A dislocation at the top grain boundary is also visible. Figure 4 clearly reveals dislocation loops (also note Fig. 5) that in some instances appear to be multiple cross-slipped screw dislocations. In this photograph and in Fig. 5 one of the dislocations has bent sharply away from the grain boundary. The grain boundary region in this photograph is producing a diffraction image with various structural details.

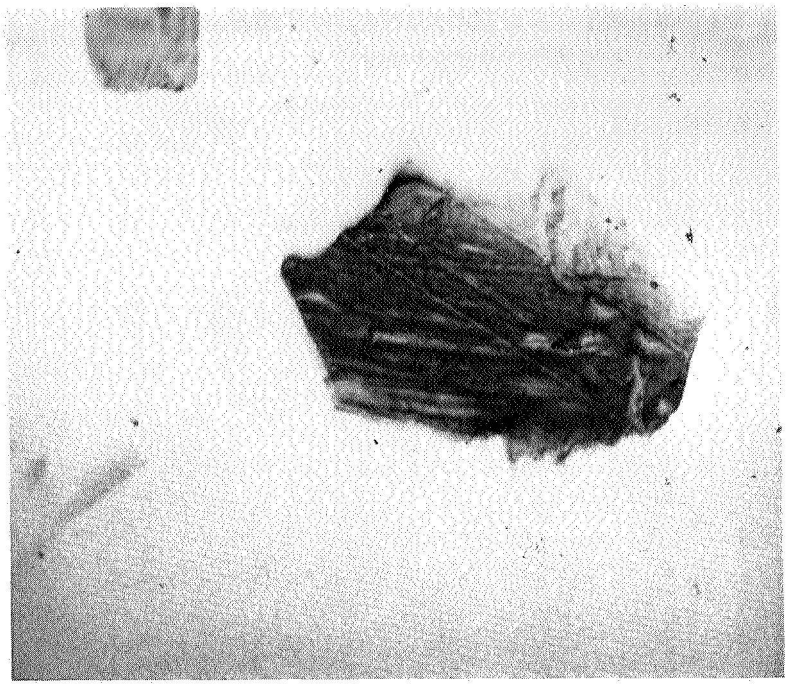


Fig. 4. X-ray micrograph showing (at upper right of grain) a diagonal edge dislocation that reflects away from grain boundary region

Fig. 5. Enlarged image of the region of Fig. 4 showing bent edge dislocation (in the upper right)

B. Preferred Orientation

Preliminary results indicated the existence of significant orientations (see Ref. 4), and attempts were made to provide quantitative results and clarify the mechanism. Existing equipment was not sufficiently precise for this purpose, and insufficient time was available for improvement.

C. Von Laue Pattern

No experimental results were obtained from the equipment. However, in preparation for such results, an existing computer program (Ref. 5) for the calculation of precision lattice parameters from such data was evaluated. Revision was made to permit greater precision, especially from the standpoint of statistical evaluation.

D. Light Microscopy

The phase contrast micrographs (Figs. 6–9) revealed that the grain boundaries contain numerous linear structures with index of refraction different from the MgO.

Some grain boundary corrugation and slip markings indicate some movement of the boundaries themselves. Polarized light examination revealed stray birefringence lines parallel to the grain boundaries.

Some preliminary measurements revealed that indeed the index of refraction of the grain boundaries varies from that of the grains themselves. In one instance the index of refraction was equal to that of Brucite.

IV. Conclusions

A. General Conclusion

In general it would appear that crystalline regions exist in the MgO grain boundaries that are separate from the grains themselves.

The bulk modulus of the grain boundary region in some instances is higher than that of MgO.

Linear dislocation structures are closely associated with the grain boundaries.

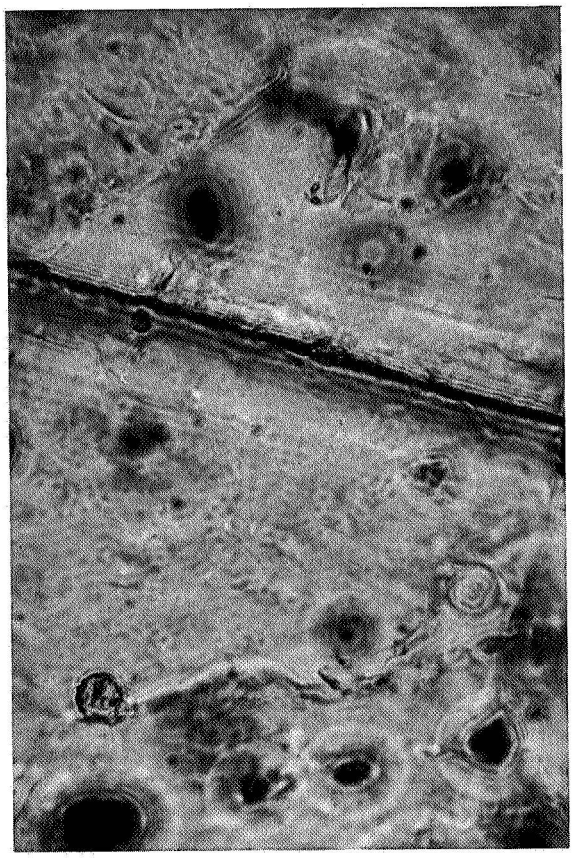


Fig. 6. Bright field image of MgO grain boundary

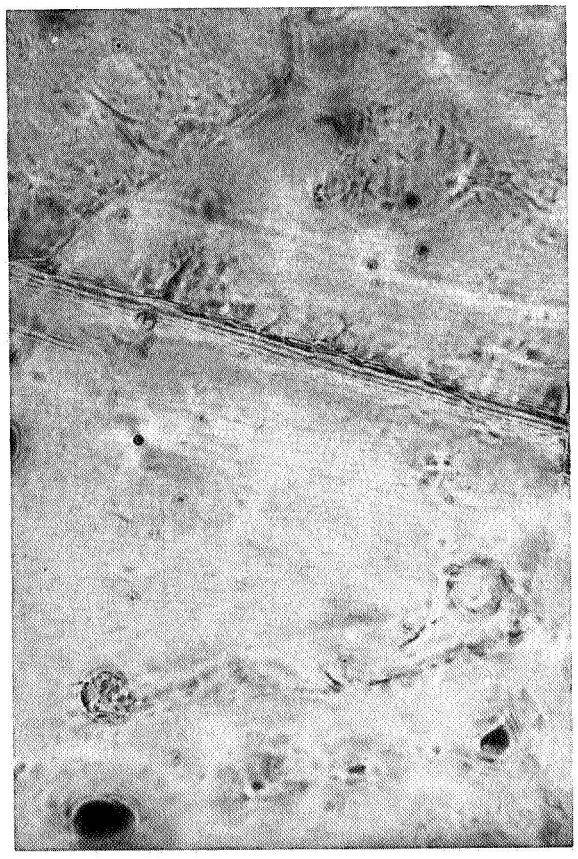


Fig. 7. Phase contrast image of MgO grain boundary

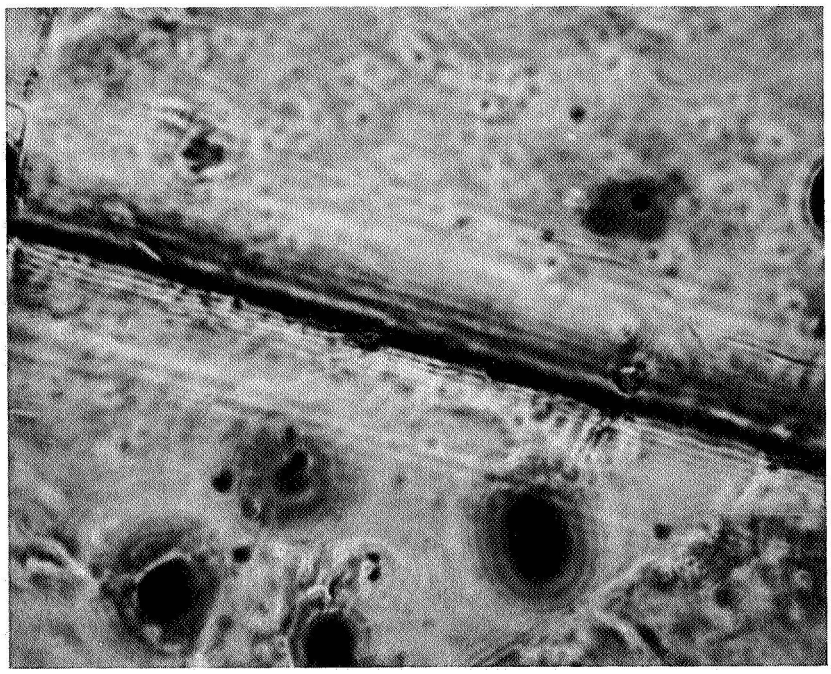


Fig. 8. Bright field image of MgO grain boundary

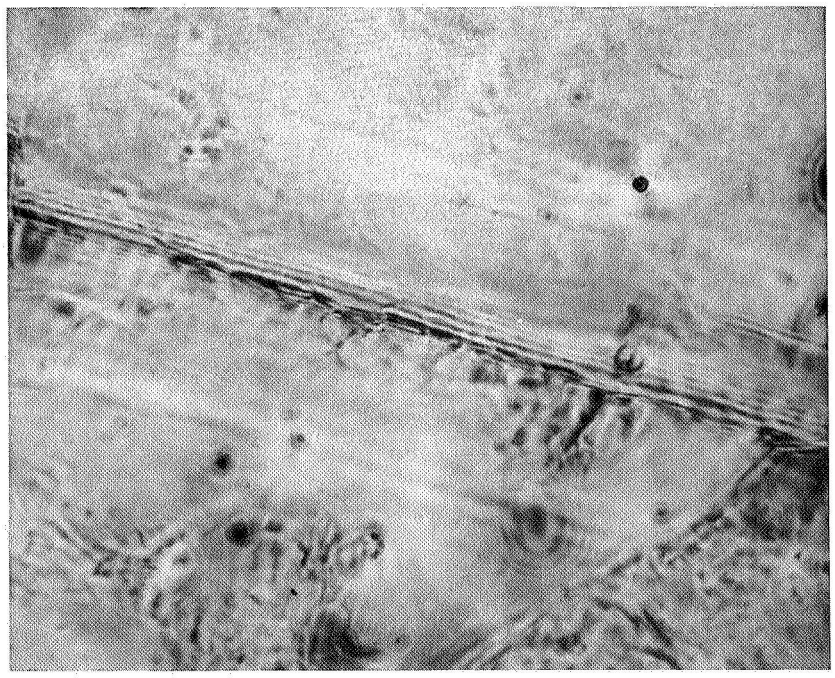


Fig. 9. Phase contrast image of MgO grain boundary

Linear-type island structures with various indices of refraction appear to be present within the grain boundary regions.

The grain boundaries examined appear to be of the low angle types.

Pole figure analysis revealed the existence of preferred (100) orientation in resintered samples.

B. Possible Future Work

The techniques used so far apparently are capable of revealing data concerning the grain boundaries and should be continued.

The planned precision micro Laue ($10\,\mu$ collimator) work should be initiated since some preliminary tests indicated that good single crystal pattern may be obtained from the individual grains within the sample. This should include various oriented micro Laue patterns of the grain boundary regions as well.

The very preliminary optical analysis clearly revealed that high-resolution phase contrast and interference techniques have a great potential for the study of grain boundaries of MgO. It was planned to add chemical microscopy techniques to the study of grain boundaries in order to reveal the presence of various impurities.

References

1. Leipold, M. H., Nielsen, T. H., de Wys, E. C., *The Effect of Grain Boundaries on the Mechanical Behavior of Ceramics,* Technical Report 32-1200. Jet Propulsion Laboratory, Pasadena, Calif., Oct. 15, 1967.
2. Leipold, M. H., "Impurity Distribution in MgO," *J. Am. Cer. Soc.*, Vol. 49, No. 9, p. 498, 1966.
3. Jorgenson, P. J., and Westbrook, J. H., "Role of Solute Segregation at Grain Boundaries During Final Stage Sintering of Alumina," *J. Am. Cer. Soc.*, Vol. 47, No. 2, pp. 63–68, 1964.
4. de Wys, E. C., and Leipold, M. H., "Indications of Preferred Orientation in Recrystallized Hot Pressed MgO," Materials Research Bulletin, Vol. 2, No. 6, pp. 591–594, June 1967.
5. Leipold, M. H., and Pauly, W. R., *7090 Program for Determination Precision Lattice Constants,* Technical Memorandum 33-109. Jet Propulsion Laboratory, Pasadena, Calif., Feb. 15, 1963.